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STIMULATED EMISSION FROM ORGANIC MOLECULES WITH POSSIBLE LASER APPLICATIONS

Review Article

(AID Work Assignment No. 43, Task 8)

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FOREWORD

This review article was prepared in response to AID Work Assignment No. 43, Task 8. It is compiled from selected papers, printed in Soviet scientific periodicals, of three Soviet conferences on luminescence and spectroscopy held in 1961 and 1962 and from issues of *Optika i spektroskopiya* of the same years; all are available at the Aerospace Information Division.

STIMULATED EMISSION FROM ORGANIC MOLECULES WITH POSSIBLE LASER APPLICATIONS

Although information on organic materials for Soviet lasers is extremely scarce, there is a large body of papers on various aspects of organic materials that may be indirectly pertinent to the central problem. A general outline is presented here of material so identified, including a sampling of the types of papers available, the type of work being done in the USSR, the manner in which it is presented, and the possible ways in which it may be related to the laser field.

Most of the material is derived from papers presented at conferences rather than papers published through other channels. This may indicate an organized attempt to push the field forward through "cross-fertilization" -- bringing scientists working on diverse problems together for discussion. This hypothesis is further supported by the opening statement made by Dr. V. L. Levshin at the Eleventh Annual Conference on Luminescence (Minsk, 10-15 September 1962), reported in the December 1962 issue of the *Vestnik* of the Academy of Sciences USSR:

> Opening the conference, Chairman of the Scientific Council on Luminescence V. L. Levshin spoke of a new form of coordination of research in the field of luminescence.... Local Council sections have been opened in Kiyev (for coordinating work done in the Ukrainian SSR), Minsk (for the Belorussian SSR), Tartu (for the Baltic republics), Irkutsk (Siberian section), and Leningrad. The sections conduct research in line with plans of the Council.

The article goes on to state that considerable attention was devoted at the conference to the new problem of developing quantum light generators.

Among the first Soviet researchers to state the problem of organic laser action in direct terms were S. G. Rautian and I. I. Sobel'man, who on 29 April 1960 submitted a paper (published in the January 1961 issue of *Optika i spektroskopiya*) on the possibility of obtaining negative absorption by electron transitions in optically pumped organic molecules. The other Soviet researchers to whom this paper refers for background material and methodology are A. P. Ivanov (who in turn refers to N. G. Bakhshiyev and B. S. Neporent), V. L. Yermolayev and K. K. Svitashev, and E. V. Shpol'skiy.

Rautian and Sobel'man present the problem as follows:

The most effective excitation of organic molecules (aromatic hydrocarbons are cited as a specific example) occurs from the singlet ground state S_0 to the other singlet states, since transitions between the singlet ground state and triplet states violate rules of selection. Nonradiative transitions from a higher singlet state S_1 populate triplet state T_1, so that a Boltzmann distribution is established among S_0, S_1, and T_1. At low temperatures (~100°K) only the lowest energy levels in S_0, S_1, and T_1 are ordinarily populated. Therefore, in the case of transitions to higher levels in S_0 from S_1 and T_1 corresponding to intensity maxima in fluorescence and phosphorescence spectra, induced emission predominates over absorption; i. e., negative absorption can take place.

Two other conditions necessary for establishing negative absorption are as follows:

1) Excited molecules must not absorb radiation of frequencies for which negative absorption is to be established. This condition is satisfied in naphthalene, anthracene, naphthacene, their halogen derivatives, etc., where the frequency of $T_1 \rightarrow T_2$ transitions is somewhat greater than that of $S_0 \rightarrow T_1$ transitions.

2) The quantum phosphorescence yield must be large. This yield, which is high for the above molecules, increases with decreased quenching time, which is in turn improved by heavy atoms in the molecules (I, Br). A high concentration of excited molecules is, of course, also necessary.

The Tenth Annual Conference on Luminescence (Moscow, 26 June to 1 July 1961) produced a number of papers pertinent to the organic laser problem. Both the opening and closing statements of Dr. Levshin cited lasers and laser applications and in fact claimed the whole field of lasers as a problem in luminescence. Levshin also presented a paper to the conference on energy migration in solutions and the association theory of luminescence quenching.

B. I. Stepanov presented a paper evaluating the present state of the theory of luminescence of complex molecules. During the discussion of Stepanov's paper, A. M. Samson presented the results of his work on the theory of luminescence quenching by additives.

A. N. Terenin and V. L. Yermolayev presented a paper on deactivation of the triplet state of aromatic molecules, and in the discussion of that paper reference was made to the work of Yermolayev with Ye. B. Sveshnikova on nonradiative energy transfer between triplet and singlet levels of organic molecules. During the same discussion D. N. Shigorin reported results he obtained in

collaboration with Yu. I. Kozlov on luminescence spectra and EPR of triphenylmethane derivatives. The importance of these papers to the organic laser problem is evident when considered in conjunction with the Rautian and Sobel'man paper.

V. A. Fabrikant, one of the top names in the Soviet gas laser field, presented a paper on Bouguer's law.

According to the opening statement by S. L. Mandel'shtam, the Fourteenth Conference on Spectroscopy (Gor'kiy, 5-12 July 1961) was to emphasize applications of spectroscopy to atomic and molecular spectral analysis. As is the current fashion in opening statements at scientific conferences, Mandel'shtam mentioned the laser as providing a stimulus to spectral analysis, as well as to "lighting the dark side of the moon." He also noted the importance to spectral analysis of the emission line spectra of organic substances at low temperatures.

The Conference heard papers by M. M. Kusakov, N. A. Shimanko, M. V. Shishkina, K. I. Zimina, and A. G. Siryuk on ultraviolet absorption spectra of aromatic hydrocarbons; by Shimanko, Shishkina, Kusakov, and V. I. Sidorenko on near-ultraviolet absorption spectra of hydrocarbons of the diphenylalkane series; by G. N. Zhizhin, Z. N. Barinova, A. L. Liberman, I. M. Kuznetsova, and N. I. Tyun'kina on infrared absorption spectra of *cis-* and *trans-* isomers of 1-methyl-2-n-alkylcyclohexanes; by M. P. Teterina and A. A. Petrov on the molar extinction factor for some absorption lines of mono-, di-, and tricyclohexylalkanes; and by A. N. Kislinskiy and Petrov on Raman spectra of some diaryl hydrocarbons (C_{20}-C_{24}) and their hydrogenation products.

These papers may be relevant in view of the recent American discovery by Gisela Eckhardt *et al.* of laser action in all ring compounds with five or more C-H or C-D bonds. Eckhardt attributes this laser action to induced Raman scattering. Although the Conference reports were published prior to Eckhardt's discovery and were not aimed at laser development, they are indicative of the state-of-the-art of a field bound to become related to lasers.

The development of organic lasers as a whole is still in such an early stage that it is difficult to judge the future significance of papers that seem pertinent today. This will become possible only in retrospect, when the field "crystallizes" sufficiently to produce working devices. Consequently, the best that can be done is to emphasize the papers of direct pertinence and to present a significant sampling of theoretical and experimental research which is only indirectly pertinent.

Several papers of indirect interest were published in *Optika i spektroskopiya* in 1962. The January issue contains a paper by Z. Simon on determination of the position of energy levels of biphenyl, phenylpyridines, and phenylpyrilium salts. The February 1962 issue contains a paper by A. M. Bogomolov on oscillation spectra of aromatic compounds, in particular para-di-substituted benzenes. (This is the 12th paper of a series by Bogomolov.)

A paper by B. Ya. Sveshnikov and V. I. Shirokov in the May issue deals with the dependence of mean duration and yield of luminescence in the quenching process on the law of molecular interaction, and a paper by H. G. Bakhshiyev, V. P. Klochkov, Neporent, and A. S. Cherkasov with absorption and fluorescence of vapors of anthracene and its derivatives. The same issue contains a paper by Levshin and Kh. I. Mamedov on fluorescence and absorption spectra of stilbene in octane at low temperatures.

The July issue contains a paper by Neporent, Bakhshiyev, V. A. Lavrov, and S. M. Korotkov on the influence of the medium on the electron spectra of complex molecules during gradual transition from vapor to solution.

Another paper of the Bogomolov series on oscillation spectra of aromatic compounds is found in the August issue, this time on characteristic oscillations of meta-substituted benzenes. This issue also contains a paper by E. V. Shpol'skiy and L. A. Klimova (the first of a series) on the line spectra of aromatic hydrocarbons in frozen crystalline solutions, particularly the first singlet-singlet transition in 3, 4-benzopyrine at 20 and 4°K. There is also a paper on EPR and absorption spectra in the visible range of alcohol and glycerine solutions of Ti^{3+} ions by N. S. Garif'yan, A. V. Danilov, and R. R. Shagidullin that may have a bearing on the development of organic host substances for lasers using paramagnetic ions.

The following month's journal contains the second paper of the Shpol'skiy and Klimova series on line spectra of polycyclic aromatic hydrocarbons in frozen crystalline solutions. This time they write in collaboration with R. I. Personov, and the paper is on singlet-singlet and triplet-singlet spectra of 1,2-benzopyrine at 77 and 4°K. The same issue contains two papers on infrared absorption spectra of organic substances.

At the Eleventh Annual Conference on Luminescence [see p. 1], in which about 370 Soviet scientists took part, the importance of lasers was again stressed. The *Vestnik* article already cited contains the following information [the papers themselves are not yet available]:

A considerable number of papers were presented on conventional lasers and laser materials and on theoretical aspects possibly relevant to organic lasers. B. I. Stepanov of the Belorussian Academy of Sciences presented a paper on oscillation in an unbounded plane-parallel layer. Cryogenic studies of luminescence in molecular crystals, luminescence caused by impurity centers, and exciton processes were reported by members of the A. F. Prikhot'ko school working under the auspices of the Ukrainian Academy of Sciences. Among these is the work of V. L. Broude, Ye. F. Shek, and M. T. Shpak on luminescence in naphthalene crystals, in which information was gained on the exciton spectrum of naphthalene through a determination of the temperature dependence of luminescence. Several papers were also presented on the Shpol'skiy effect of transformation of narrow-band emission spectra of organic compounds in frozen paraffin solutions at liquid-nitrogen and helium temperatures into quasi-line spectra usually with the same frequencies as those in Raman and lattice-impurity spectra. This was interpreted as a type of Mössbauer effect.

Levshin himself presented a paper on energy migration during excitation and damping in associated solutions. Sveshnikov presented a paper on the diffusion theory of fluorescence quenching in solutions by impurities. A. N. Sevchenko, V. V. Kuznetsova, and V. S. Khomenko presented a paper on migration of excitation energy in organic crystals containing rare earths. D. N. Shigorin *et al.* presented a paper on an EPR spectrometer study of aromatic hydrocarbons, in which they discovered relationships between triplet state lifetimes and molecular structure. V. V. Zelinskiy *et al.* proved the existence of a relationship between the luminescence yield of complex molecules in solutions and the nature of their spectra. Neporent and O. V. Stolbovaya described an orientation effect of molecules in solutions under the action of polarized light.

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